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Equation of state for chains in Statistical Associating Fluid Theory —Dimer

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Abstract : The SAFT-Dimer (SAFT-D) theory is reformulated to yield improved equation of state for hard sphere chain fluid. Two sets of the equation of state are proposed by employing Chiew's expressions for the contact values of m hard sphere site-site correlation function $g(\sigma)$. Comparison with molecular simulation data shows that improved SAFT-D equation of state predicts compressibility factor more accurately than Ghonasgi and Chapman's equation of state. It has been shown that SAFT-Dimer theory can be easily applied to fused hard sphere chain fluids by considering the correct value of effective chain length (m^*). The SAFT-Dimer theory is also extended to the two dimensional tangent and fused hard disk chain fluids. For the fused hard disk dimer fluid, SAFT equation of state is found to be more accurate than the Boublik hard disk dimer equation of state. For tangent hard disk chain fluids, the results obtained from SAFT-Dimer theory are compared with Monte Carlo results for 5 mers and with GFD theory for 4 mers, 8 mers and 16 mers.

Keywords : SAFT-D theory, hard sphere chain fluids, hard disk chain fluids.

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1. Introduction

The study of the equation of state for the homonuclear hard sphere chain fluid has received much attention in recent years. There have been several theories for predicting the equation of state of the linear chain molecules such as perturbation theories [1–3], the Percus-Yevick (PY) theory [4], the generalized flory dimer theory (GFD) [5] and the statistical associating fluid theory (SAFT) [6]. The advantage of the SAFT theory is that it requires the equation of state of the monomer only. The SAFT equation of state has been in good agreement for short chains and become worse for the longer chain molecules. Thus, it is improved by Ghonasgi and Chapman [7], and is called the SAFT-D theory. The equation of state in SAFT-D theory requires only the contact values of the hard spheres and hard dispheres site-site correlation functions. The theory can be easily applied to the molecules having longer chain length. The present work re-examines the equation of state of the SAFT-D theory. The theory employed the contact value of the correlation function $g(\sigma)$ of the dimer proposed by Chiew [8]. Chiew [8] has derived the two analytic expressions for average correlation function at contact as a function of chain length m and hard sphere site volume fraction η. Ghonasgi and Chapman [7] have employed the expression for $g(\sigma)$ of the dimer with an assumption that the correlation function at contact of the dimer, tetramer, octamer and so on, will remain same. In this paper, we have applied both the expressions of $g(\sigma)$ for m components separately without making any assumption. We have found that the equations of state obtained by using both the expressions of $g(\sigma)$ predict better results than those obtained by Ghonasgi and Chapman. The theory has been applied to the tangent hard sphere chains and also to the fused hard sphere linear chain. Considering the correct value of the chain length m, the SAFT-D theory predicts good results for the compressibility factor of the fused hard sphere chain molecules.

Unfortunately, two dimensional hard body systems are not as extensively studied as three dimensional hard body fluids even if it is useful to understand the behaviour of surface layers. So far, the interest has been focussed on the study of the hard disk dimer fluids [9]. Recently, Zhou *et al* [10] have extended the thermodynamic perturbation theory called TPT1-AB and calculated the equation of state of the fused hard disk (FHD) dimer fluids. Honnell and Hall [5] have successfully applied the generalized flory theory (GFD) for the 5 mers tangent hard disk fluids. In the present work, we have extended the SAFT and SAFT-D theory to two

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dimensional hard body fluids. The SAFT theory is applied to determine the equation of state of the fused hard disk dimer fluid while the SAFT-D theory is applied to predict the equation of state of higher mers fluids *i.e.* 4 mers, 5 mers, 8 mers and 16 mers. The results are compared with Monte Carlo simulation for 5 mers [11]. In the absence of Monte Carlo simulation values for higher mers, we have compared our results with GFD theory which is supposed to be a sufficiently accurate theory to predict equation of state of the chain fluids.

2. Theory

A. Hard sphere chain fluid :

Let us consider the even numbered pair of the m hard spheres. The equation of state of the disphere in SAFT theory can be written as

$$Z^{HD} = 2Z^{HS} - \left(1 + \eta \frac{\partial \ln g_{HS}(\sigma)}{\partial \eta}\right). \tag{1}$$

The pair of dispheres can form chain which have four segments *i.e.* tetramers. In SAFT-D theory (eq. 9 of ref. [7]), the equation of state for tetramer is given by

$$Z^{HT} = 2Z^{HD} - \left(1 + \eta \frac{\partial \ln g_{HD}(\sigma)}{\partial \eta}\right). \tag{2}$$

Similarly, the equations of state for Octamers (Z^{HO}) 16 mers ($Z^{HS\alpha}$) and 32 mers (Z^{32}) can be written as

$$Z^{HO} = 2Z^{HT} - \left(1 + \eta \frac{\partial \ln g_{HT}(\sigma)}{\partial \eta}\right), \tag{3}$$

$$Z^{HS\alpha} = 2Z^{HO} - \left(1 + \eta \frac{\partial \ln g_{HO}(\sigma)}{\partial \eta}\right), \tag{4}$$

$$Z^{32} = 2Z^{HS\alpha} - \left(1 + \eta \frac{\partial \ln g_{HS\alpha}(\sigma)}{\partial \eta}\right) \tag{5}$$

The equation of state for 32 mers can be solved as

$$\begin{aligned} Z^{32} = {} & 32Z^{HS} - 16\left(1 + \eta \frac{\partial \ln g_{HS}(\sigma)}{\partial \eta}\right) \\ & - 8\left(1 + \eta \frac{\partial \ln g_{HD}(\sigma)}{\partial \eta}\right) - 4\left(1 + \eta \frac{\partial \ln g_{HT}(\sigma)}{\partial \eta}\right) \\ & - 2\left(1 + \eta \frac{\partial \ln g_{HO}(\sigma)}{\partial \eta}\right) - \left(1 + \eta \frac{\partial \ln g_{HS\alpha}(\sigma)}{\partial \eta}\right). \end{aligned} \tag{6}$$

A general expression can be written as

$$\begin{aligned} Z^{m} = {} & mZ^{HS} - (m-1) - \eta\left\{\frac{m}{2}\frac{\partial \ln g_{HS}(\sigma)}{\partial \eta}\right. \\ & + \frac{m}{4}\frac{\partial \ln g_{HD}(\sigma)}{\partial \eta} + \frac{m}{8}\frac{\partial \ln g_{HT}(\sigma)}{\partial \eta} \\ & \left. + \frac{m}{16}\frac{\partial \ln g_{HO}(\sigma)}{\partial \eta} + \frac{m}{32}\frac{\partial \ln g_{HS\alpha}(\sigma)}{\partial \eta}\right\}. \end{aligned} \tag{7}$$

The equation of state for 4, 8 and 16 mers can be written by taking into account the terms up to $\frac{m}{x} = 1$. The eq. (7) can be further solved for the two values of $g(\sigma)$ proposed by Chiew [8]. The two values $g_1(\sigma)$ and $g_2(\sigma)$ are as follows :

$$g_1(\sigma) = \frac{2 + (3m-2)\eta}{2m(1-\eta)^2}, \tag{8a}$$

$$g_2(\sigma) = \frac{(m+2) + (5m-2)\eta}{4m(1-\eta)^2}. \tag{8b}$$

Both the equations predict the same value of $g(\sigma)$ for disphere but different values for higher m-mers. For $g_1(\sigma)$, the equation of state can be solved as

$$\begin{aligned} Z^{m} = {} & mZ^{HS} - (m-1) - \left(\frac{\eta}{1-\eta}\right)\left\{\frac{m}{2}\frac{(5-2\eta)}{(2-\eta)} + \frac{m}{4}\frac{2(2+\eta)}{(1+2\eta)}\right. \\ & \left. + \frac{m}{8}\frac{(7+5\eta)}{(1+5\eta)} + \frac{m}{16}\frac{(13+11\eta)}{(1+11\eta)} + \frac{m}{32}\frac{(49+47\eta)}{(1+47\eta)}\right\}. \end{aligned} \tag{9}$$

For $g_2(\sigma)$, the equation of state can be solved as

$$\begin{aligned} Z^{m} = {} & mZ^{HS} - (m-1) - \frac{\eta}{1-\eta}\left\{\frac{m}{2}\frac{(5-2\eta)}{(2-\eta)} + \frac{m}{4}\frac{2(2+\eta)}{(1+2\eta)}\right. \\ & \left. + \frac{m}{8}\frac{(5+3\eta)}{(1+3\eta)} + \frac{m}{16}\frac{(29+19\eta)}{(5+19\eta)} + \frac{m}{32}\frac{(113+79\eta)}{(17+79\eta)}\right\}. \end{aligned} \tag{10}$$

Recently, Chang and Sandler [12] have proposed the correlation function at contact for homonuclear hard sphere chain fluid using the Wertheim integral equation theory as

$$g(\sigma) = \frac{(1+\eta/2)}{(1-\eta)^2} - \frac{(m-1)}{m}\frac{1}{(1-\eta)}. \tag{11}$$

That gives the same expression for contact value of $g(\sigma)$ as given by $g_1(\sigma)$ up to 16 mers. The last term for 32 mers in eq. (9) is changed to $\left(\frac{25+23\eta}{1+23\eta}\right)$; however, the magnitude remains close to that obtained in eq. (9). Thus, the equations of state obtained by using $g(\sigma)$ proposed by Chang and Sandler, predict the same values as those obtained by eq. (9) up to 32 mers.

For comparison, we have also calculated the equation of state proposed by Ghonasgi and Chapman [7] derived by assuming $\frac{\partial \ln g_{HT}(\sigma)}{\partial \eta} = \partial \ln g_{HD}(\sigma)/\partial \eta$ as

$$\begin{aligned} Z^{m} = {} & mZ^{HS} - \frac{m}{2}\left(1 + \frac{(5-2\eta)\eta}{(1-\eta)(2-\eta)}\right) \\ & - \left(\frac{m}{2} - 1\right)\left(1 + \frac{2\eta(2+\eta)}{(1-\eta)(1+2\eta)}\right). \end{aligned} \tag{12}$$

B. Hard disk chain fluid :

Let us first examine the SAFT theory for fused hard dimer fluid. The equation of state (Z^{HDD}) for hard dumbell fluid can be written as

$$Z^{HDD} = mZ^{HD} - (m-1)\left[1 + \eta \frac{\partial \ln g_{HD}(\sigma)}{\partial \eta}\right], \quad (13)$$

where Z^{HD} is the equation of state of hard disk and $g_{HD}(\sigma)$ is the hard disk contact value of the pair correlation function. The equation of state of the monomer [13,5] can be written as

$$Z^{HD} = \frac{1+.112\eta^2}{(1-\eta)^2}, \quad (14)$$

where η is the area fraction depending on the chain number density (ρ_{ch}) and the chain area (A_{ch}) such that $\eta = (\rho_{ch})(A_{ch})$. The hard disk contact value can be obtained as

$$Z^{HD} = 1 + 2\eta g_{HD}(\sigma); \quad (15)$$

hence,

$$g_{HD}(\sigma) = (1 - 0.444\eta)/(1-\eta)^2. \quad (16)$$

The effective chain length, considering straight chain in AB approximation, can be obtained as [10]

$$m = \frac{\left[m\pi - 2(m-1)\cos^{-1}(l^*)\right]^2}{\pi\left\{m\pi - 2(m-1)\left[\cos^{-1}(l^*) - l^*\sqrt{1-(l^*)^2}\right]\right\}}. \quad (17)$$

Thus, the final equation for fused hard disk dimer fluid can be written as

$$Z^{HDD} = m^* \frac{(1+.112\eta^2)}{(1-\eta)^2} - (m^*-1)\left\{1 + \frac{\eta}{1-\eta}\left(\frac{1.556-.444\eta}{1-.444\eta}\right)\right\}. \quad (18)$$

We now derive an expression for tangent hard disk chain fluid. The equation of state for tangent hard disk fluid can be derived in a way similar to that for three dimensional chain fluid

$$Z^{mD} = mZ^{HD} - \frac{m}{2}\left[1 + \eta \frac{\partial \ln g_{HD}(\sigma)}{\partial \eta}\right] - \left(\frac{m}{2} - 1\right)\left(1 + \eta \frac{\partial \ln g_{HDD}(\sigma)}{\partial \eta}\right), \quad (19)$$

where $g_{HDD}(\sigma)$ is the contact value of the pair correlation function for the hard disk dimer fluid. The equation of state of the hard disk dimer is recently proposed by Boublik [9] as

$$Z^{HDD} = \frac{1 + (\gamma - 1)\eta' + \gamma^2\eta'^2/8}{(1-\eta')^2}, \quad (20)$$

where γ is the two dimensional shape factor which depends on the area and perimeter of the molecule, η' is the area fraction of the dimer disk. The values of γ and η' are determined by Honnell and Hall [5] as $\gamma = 1.3211$ and $\eta' = 1.051\eta$. The eq. (20) can be used to determine the contact value of the correlation function for dimer disk fluid as

$$Z^{HDD} = 1 + 2\eta' n^* g_{HDD}(\sigma), \quad (21)$$

where n^* is a numerical quantity. We are encouraged to write eq. (21) as Curro [14] and Honnell *et al* [15] have suggested that pressure equation for linear chain may be written solely in term of site-site correlation functions and the resulting expression for equation of state has the same general form as the monoatomic equation.

Hence, $$g_{HDD}(\sigma) = \frac{(\gamma+1)2 + \frac{\overline{16}}{} - \frac{\div}{\gamma}|\eta}{n^*(1-\eta')^2} \quad (22)$$

and

$$\frac{\partial \ln g_{HDD}(\sigma)}{\partial \eta} = \frac{\overline{16}}{\overline{(\gamma+1)} \perp \left(\frac{\gamma^2}{16} - \frac{1}{2}\right)|\eta'} \cdot \overline{(1-\eta')} \quad (23)$$

The final expression of the equation of state for tangent hard disk chain fluid can be written as

$$Z^{mD} = mZ^{HD} - \frac{m}{2}\left\{1 + \left(\frac{\eta}{1-\eta}\right)\left(\frac{1.556-.444\eta}{1-.444\eta}\right)\right\} - \left(\frac{m}{2} - 1\right)\left[1 + \eta\left|\frac{\frac{\gamma^2}{16} - \frac{1}{2}}{\frac{(\gamma+1)}{2} + \left|\frac{\gamma^2}{16} - \frac{1}{2}\right|\eta'}\right.\right](1-\eta') \quad (24)$$

3. Results and discussion

(i) Homonuclear hard sphere tangent chain molecules :

The equations of state predicted by the SAFT-D theory using eqs. (9) and (10) are compared with molecular simulation data [16–18] for homonuclear hard sphere chain of 8 mers and 16 mers. The values obtained by eq. (12) are also shown in Table 1. The compressibility factor for 4 mers will remain same in all the three cases *i.e.* eqs. (9), (10) and (12). We find that the eqs. (9) and (10) predict better agreement with simulation data [16–18] in comparison to the values obtained by Ghonasgi and Chapman's equation state *i.e.*, eq. (12). The data in Table 1 clearly indicate that eq. (12) over estimates the compressibility factor at all densities. It is due to the assumption $\frac{\partial \ln g_{HO}(\sigma)}{\partial \eta} = \frac{\partial \ln g_{HT}(\sigma)}{\partial \eta} = \frac{\partial \ln g_{HD}(\sigma)}{\partial \eta}$ made by them. Among eqs. (9) and (10), eq. (10) seems to predict better results for higher mers particularly for 32 mers, as shown in Table 2.

Table 1. Comparison of our equations of state for m hard sphere chain fluids with eq (12) and with the simulation data (16–18) ($\rho^* = m\rho\sigma^3 = 6\eta/\pi$).

	Z^m							
	8 mers				16 mers			
ρ^*	Eq (9)	Eq.(10)	Eq.(12)	Simulation	Eq (9)	Eq.(10)	Eq (12)	Simulation
0 1	1 63	1 71	1 74	1.76	1 79	2 21	2.29	2 25
0.2	2.85	2 96	3 02	2 99	3 93	4 39	4 64	4 47
0 3	4 80	4 92	5 00	4.91	7 60	8 09	8.39	8 09
0.4	7.74	7 86	7.96	7 75	13 26	13 76	14 09	13 59
0.5	12 06	12.19	12 29	11 95	21.68	22 17	22 52	21 96
0 6	18.89	18 51	18 61	18.26	34.08	34 56	34 92	34.05
0 7	27 67	27.79	27.90	27 14	52.38	52 85	53 21	51 80
0 8	41.49	41 61	41 72	40 85	79 72	80 17	80 53	81 28
0.9	62 48	62 60	62 71	62.03	121.35	121 78	122 14	

Table 2. Comparison of the equations of state of 32 mers hard sphere chains with molecular simulation-as a function of reduced density ρ^*

	Z^m				
ρ^*	Eq. (9)	Eq (10)	Eq. (12)	Simulation	GFD [5]
0.191	5.32	6 73	7 36	7.08	8 62
0 382	21 72	23.15	24 00	23.00	25 26
0.478	36.48	37.80	38.75	37 00	39.47
0.573	57 70	58 99	59.94	57 60	59 63

(ii) Fused hard sphere chain molecules :

We have applied the SAFT-D theory to the fused hard sphere chain molecules. We consider the eq. (10) to describe the equation of state of fused hard sphere chain. To do that in the SAFT-D theory, let us introduce the modified chain length to the fused hard sphere chain instead of the simple hard sphere chain length. Consider the effective number of dimers per chain to be m^* and the dimer diameter is d. Thus, the surface area (S_m) and volume (V_m) of a fused hard sphere chain can be written as

$$V_m = m^* \quad \frac{3}{-}\left[1+\frac{3}{2}\left(\frac{l}{d}\right)-\frac{1}{2}\left(\frac{l}{d}\right)^3\right], \tag{25}$$

$$S_m = m^*\pi d^2\left[1+\left(\frac{l}{d}\right)\right], \tag{26}$$

$$= \left(\frac{}{36\pi V_m^2}\right. \frac{\left[1+\frac{3}{2}\left(\frac{l}{d}\right)-\frac{1}{2}\left(\frac{l}{d}\right)^3\right]^2}{\left[1+\left(\frac{l}{d}\right)\right]^3}. \tag{27}$$

Now, replacing m by m^* in eq. (10), we calculate the equation of state of the fused hard sphere chain of 4 mers, 8 mers and 16 mers at the reduced bond length $l^* = (l/d)$ and

Table 3. The parameters used in the calculations of fused hard sphere cahins

Mers	l^*	V_m	S_m	m^*
4	0.3664	1.422	6.905	1.311
8	0.3330	2.575	11.728	1.992
16	0 3195	4 920	21.547	3.404

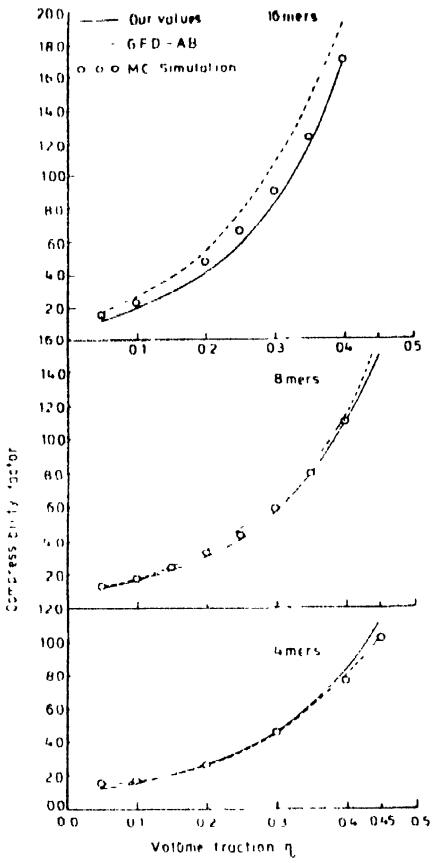

Figure 1. Compressibility factor *versus* volume fraction for 4 mers, 8 mers and 16 mers, our values (SAFT-D theory)—solid line, GFD theory in AB approximation dotted line and Mc simulation results open circles

at the effective volume fraction η varying from 0.05 to 0.45. The values of l^*, S_m, V_m and m^* are presented in Table 3. We find that the SAFT-D theory adequately predicts the compressibility factor at all densities. The results are plotted in Figure 1 for 4 mers, 8 mers and 16 mers and are compared with the results fo GFD theory [19] in AB approximation and the simulation data [19]. Figure 1 reveals that the SAFT-D theory (present work) under estimates and GFD theory over estimates the compressibility factor as compared to the simulation results. This discrepancy is almost negligible for 4 mers but increases with bond length. However, our results are

more close to simulation results than those of GFD theory in AB approximation for higher bond lengths *i.e.* for 8 mers and 16 mers.

(iii) Fused hard disk dimer fluid :

In Table 4, we compare the compressibility factor predicted by SAFT theory [eq. (18)] for the fused hard disk dimer fluid with the compressibility factor of Boublik [9], Zhou *et al* [10] (TPT1-AB) and with the Monte Carlo simulation [20] at reduced bond length (l^*) ranging from 0.1 to 0.9 and at various reduced densities ρ^*. The SAFT equation of state, similar to TPT1-AB shows remarkable improvement over Boublik hard disk dimer equation of state, particularly for tangent hard disk dimers at high density ($\rho^* = .4$).

Table 4. Comparison between the compressibility factors predicted by SAFT-AB (ours), Boublik [9], TPT1-AB [10] and those obtained by Monte Carlo Simulation [20] for fused hard disk dimer fluids.

l^*	ρ^*	Boublik	TPT1-AB	SAFT-AB	Mc
0.3	0.3	2.24	2.23	2.23	2.22
	0.4	3.23	3.20	3.19	3.16
	0.5	5.01	4.94	4.95	4.94
	0.6	8.74	8.50	8.62	8.41
0.5	0.3	2.74	2.70	2.70	2.71
	0.4	4.45	4.35	4.35	4.35
	0.5	8.32	8.00	8.09	8.09
0.7	0.3	3.41	3.31	3.31	3.39
	0.4	6.38	6.09	6.11	6.35
	0.5	15.34	13.98	14.37	15.09
1.0	0.2	2.52	2.55	2.54	2.52
	0.3	4.76	4.83	4.81	4.75
	0.4	11.35	11.05	11.08	11.04

(iv) Freely jointed hard disk chain fluids :

For two-dimensional freely jointed chain fluids, the Monte Carlo simulation results are available only for 5 mers [11].

Table 5. Comparison between SAFT-D equation of state [eq. (24)] and the equations of state predicted by GFD theory for tangent hard disc chain fluid.

	Z^{mD} (SAFT-D)			Z^{mD} (GFD)		
η	4 mers	8 mers	16 mers	4 mers	8 mers	16 mers
0.1	1.405	1.623	2.058	1.405	1.626	2.069
0.2	2.038	2.643	3.853	2.030	2.629	2.833
0.3	3.075	4.387	7.011	3.035	4.313	6.868
0.4	4.852	7.480	12.737	4.769	7.314	12.417
0.5	8.115	13.327	23.750	8.040	13.199	23.513

We have calculated the equation of state of 5 mers using SAFT-D theory [eq. (24)] and have compared it with the Monte Carlo simulation in Figure 2. We find a good agreement with simulation results as obtained for GFD theory [5]. The equation of state of 5 mers for SAFT-D theory (eq. 24) and GFD theory overlap each other.

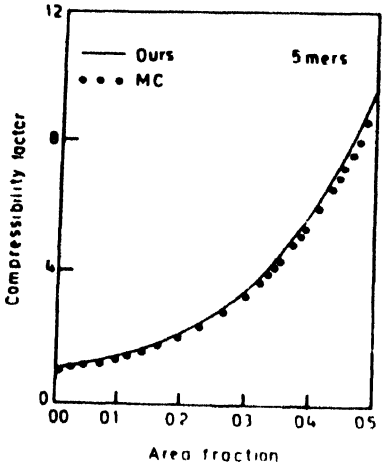

Figure 2. Compressibility factor *versus* area fraction for two dimensional freely jointed 5 mers, our values (SAFT-D theory)—solid line, Mc simulation solid circles.

The equation of state in GFD theory are calculated using eqs. (24) to (28) from the work of Honnell and Hall [5]. To get confidence in our work, we further calculated the equation of state for 4 mers, 8 mers and 16 mers and compared with those obtained by GFD theory [5]. We find that two results are very close to each other as shown in Table 5.

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